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Photoinduced Conversion of Silver Nanospheres to Nanoprisms

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A photoinduced method for converting large quantities of silver nanospheres into triangular nanoprisms is reported. The photo-process has been characterized by time-dependent ultraviolet-visible spectroscopy and transmission electron microscopy, allowing for the observation of several key intermediates in and characteristics of the conversion process. This light-driven process results in a colloid with distinctive optical properties that directly relate to the nanoparticle shape of the silver nanospheres. Theoretical calculations coupled with experimental observations allow for the assignment of the nanoparticle plasmon bands and for the first identification of two distinct quadrupole plasmon resonances for a nanoparticle. Unlike the spherical particles they are derived from, Rayleigh light-scatter in the blue, these nanoprisms exhibit scattering in the red, which could be useful in developing multicolor diagnostic labels on the basis not only of nanoparticle composition and size but also of shape.

Size provides important control over many of the physical and chemical properties of nanoscale materials, including luminescence, conductivity, and catalytic activity (1, 2). Colloidal chemists have gained excellent control over particle size for several spherical metal and semiconductor compositions, which has led to the discovery of quantum confinement in colloidal nanocrystals and to the use of such structures as probes for biological diagnostic applications, LED materials, lasers, and Raman spectroscopy—enhancing materials (3–10). However, the challenge of synthetically controlling particle shape has been met with limited success. Nevertheless, some physical and solid-state chemical deposition methods have been developed for making semiconductor and metal nanowires, nanobelts, and nanodots (11–13). Now, there are also a variety of methods for making rods with somewhat controllable aspect ratios using seedling approaches (14, 15) and electrochemical (16, 17) and membrane-templated syntheses (18). Less is known about bulk solution synthetic methods for nonspherical particles, although methods do exist for making colloidal samples of Pt cubes and pyramids (19) and PbSe, CdS, and Ni triangles (20–22). Trace quantities of Au and Ag nanoparticles have been observed as by-products of methods that predominantly produce spheres (23, 24). Promising recent work has resulted in methods for synthesizing BaCrO₄, CdS, and Co nanorods and distributions of arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals (25–28).

All of these solution methods are based on thermal processes, and, in most cases with the exception of rods, they yield relatively small quantities of the desired particle shape. Thus, the development of bulk solution synthetic methods that offer shape control is of paramount importance if the full potential of these materials is to be realized. Herein, we report a photoinduced method for synthesizing large quantities of silver nanoparticles in high yield in the form of a colloidal suspension. This photo-mediated route has led to a colloid with distinctive optical properties that directly relate to the shape control. In a typical experiment, spherical silver particles were prepared by injection of NaBH₄ solution (50 mM, 1 ml) to an aqueous solution of AgNO₃ (0.1 mM, 100 ml) in the presence of trisodium citrate (0.3 mM). Bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt solution (50 mM, 1 ml) was subsequently added by dropwise addition to the solution as a particle stabilizing agent. The system is then irradiated with a conventional 40-W fluorescent light source.
and its concentration, the ligand ratio of BSPP to citrate, and light. The reaction is initiated by light at wavelengths between 350 to 700 nm. The conversion does not take place in the dark (over a 2-month time period) or when irradiated with near-infrared light (>700 nm, 40-W fluorescent tube light source with a cutoff filter). Therefore, the reaction, which results in nanoprisms, can be selectively turned on or off simply by controlling the exposure of the colloid to light of the appropriate wavelength. The rate of the reaction decreases as a function of increasing ratio of BSPP to citrate (range 0.01 to 1); however, nanoprisms form over the entire ligand ratio range. Optimum results were obtained with a 0.3:1 ratio. Comparable results are also obtained with spherical particles formed from AgClO₄.

We have identified three distinctive stages in nanoprism formation: induction, growth, and termination (Fig. 1B). Detailed TEM studies revealed that during the induction period extremely small spherical silver clusters (2 to 4 nm) were formed, which were not observed in the solution containing the initial spherical particles. These silver clusters may have formed from either fragmentation or dissolution of the larger particles. Photoinduced fragmentation of silver nanoparticles (visible laser at 532 nm) has been observed by Hartland and co-workers (29), albeit with a much higher intensity source. The small nanoprisms (5- to 10-nm edge lengths; Fig. 2B, arrow) observed herein form concurrently with the formation of these small clusters. The silver nanoprisms then act as seeds and grow as the small spherical crystals are digested (Scheme 1). Once the spherical particles and small nanoclusters are consumed, the reaction terminates. The photoinduced conversion of silver particles into small clusters makes the use of light an efficient way to control the growth of the silver nanoprisms. Other researchers have used visible lasers, UV, or γ irradiation to prepare spherical silver nanocrystals from silver salts in the presence of organic reducing agents (30, 31), and, typically, photoinduced reduction mechanisms are invoked to describe such processes. Such mechanisms are different than the growth mechanism proposed herein for the silver nanoprisms in which the spherical silver particles begin in the reduced state and are exclusively transformed into nanoprisms through the light-induced ripening process.

TEM images and electron energy loss spectroscopy analysis (EELS) show that the particles formed in this unusual reaction are indeed silver nanoprisms, not triangular tetrahedra (Fig. 3). The triangular thickness fringes expected for triangular tetrahedra are not observed in the TEM. The EELS data show that each nanoprism has a flat top and bottom (Fig. 3A). Upon evaporation of solvent, the silver nanoprisms assemble into “stacks” on the TEM grids (Fig. 3B), which allow precise measure-
mment of their thickness (15.6 ± 1.4 nm). These stacks appear as nanorods in the two-dimen-
sional TEM images, but tilting experiments confirm that they are nanoprismos. Each nano-
prism is a single crystal with a lattice spacing of 1.44 Å, as shown by electron diffraction anal-
ysis (Fig. 3C). Detailed TEM investigations (tilting diffraction with three zone axes) of in-
dividual silver nanoprismos have shown that the 1.44 Å lattice spacing corresponds to Bragg
diffraction from their [220] lattice planes [face-
centered cubic (fcc)]. Therefore, the top crystal
face of each nanoprism must be (111). An addi-
tional set of relatively weak spots in the diffraction pattern, corresponding to \( \{222\} \) with a 2.5 Å spacing (23), is also observed. These weak diffraction spots derive from the
local hexagonal-like structure observable only for a silver (or gold) sample that is atomically
flat (32, 33). Taken together, these data are consistent with the structural characterization of
these previously unknown particles as thin nanoprismos with atomically flat tops and
bottoms.

The large structural anisotropy of these tri-
angular nanoprismos should substantially influ-
ence their optical properties, including light-
absorption, -scattering, and surface-enhanced Raman spectroscopy (SERS). According to Mie
theory (34), small spherical nanocrystal—eit-
er Ag or Au—should exhibit a single surface
plasmon band, whereas anisotropic particles should exhibit two or three bands, depending on
their shape. Larger particles can exhibit addi-
tional bands, corresponding to quadrupole and
higher multipole plasmon excitation. To charac-
terize the extinction spectrum in Fig. 1A(d), we have solved Maxwell’s equations for light inter-
acting with a triangular prism using a finite
element–based method known as the discrete dipole approximation (DDA) (35). The shape and
dimensions of the nanoprism (depicted in Fig.
4A) are average representations of the tri-
angular prisms observed in the TEM images (Fig.
2D). Three bands were observed that qual-
itatively match the wavelengths of the measured
spectra [compare Fig. 1A(d) and Fig. 4A]. Ex-
amination of the induced polarizations associ-
ated with these peaks indicates that the 770-nm
peak is the in-plane dipole plasmon resonance,
the 470-nm peak is the in-plane quadrupole resonance, and the 340-nm peak is the out-of-
plane quadrupole resonance. The out-of-plane
dipole resonance at 410 nm is sufficiently weak and broad that it is barely discernable as a
shoulder on the 470-nm peak. Additional calcu-
lations indicate that the peak at 770 nm is very
sensitive to the sharpness of the tips on the
triangles. For example, if a 12-nm region at each
tip of a prism is removed, the long-wavelength resonance at 770 nm for the perfect prism shifts
to 670 nm without changing the other resonances
(Fig. 4B). Note that TEM shows that about
10% of the prisms are truncated (Fig. 2D). Therefore, these calculations not only allow us
to identify the important features in the spec-
trum of the nanoprismos but also the subtle rela-
tion between particle shape and the frequency of
the bands that make up their spectra.

These novel nanostructures are unusual and
their optical properties are striking. For ex-
ample, they have provided the first observation of
two distinct quadrupole plasmon resonances for
a nanoparticle. Unlike the spherical particles from which they are derived that scatter in the
blue, they exhibit Rayleigh scattering in the red
(Fig. 5A). Light-scattering of metal nanoparticle
probes already has been exploited in the devel-
opment of many biodiagnostic applications (36,
37). Although conventional spherical particles
made of gold or silver do not scatter in the red,
their scattering properties can be tailored by
adjusting their size and composition (Fig. 5, B
through E). Therefore, the discovery of these
previously unknown nanoprismos and their un-
usual optical properties points to a way of de-
veloping multicolor labels on the basis of nano-
particle shape in addition to composition and
size. Lastly, the light-scattering properties of
these materials are simply one consequence of
controlling particle shape. Indeed, theoretical
calculations have predicted that silver nano-
prismos should have enormous SERS enhance-
ment factors and second harmonic generation
capabilities (10, 35).

References and Notes
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